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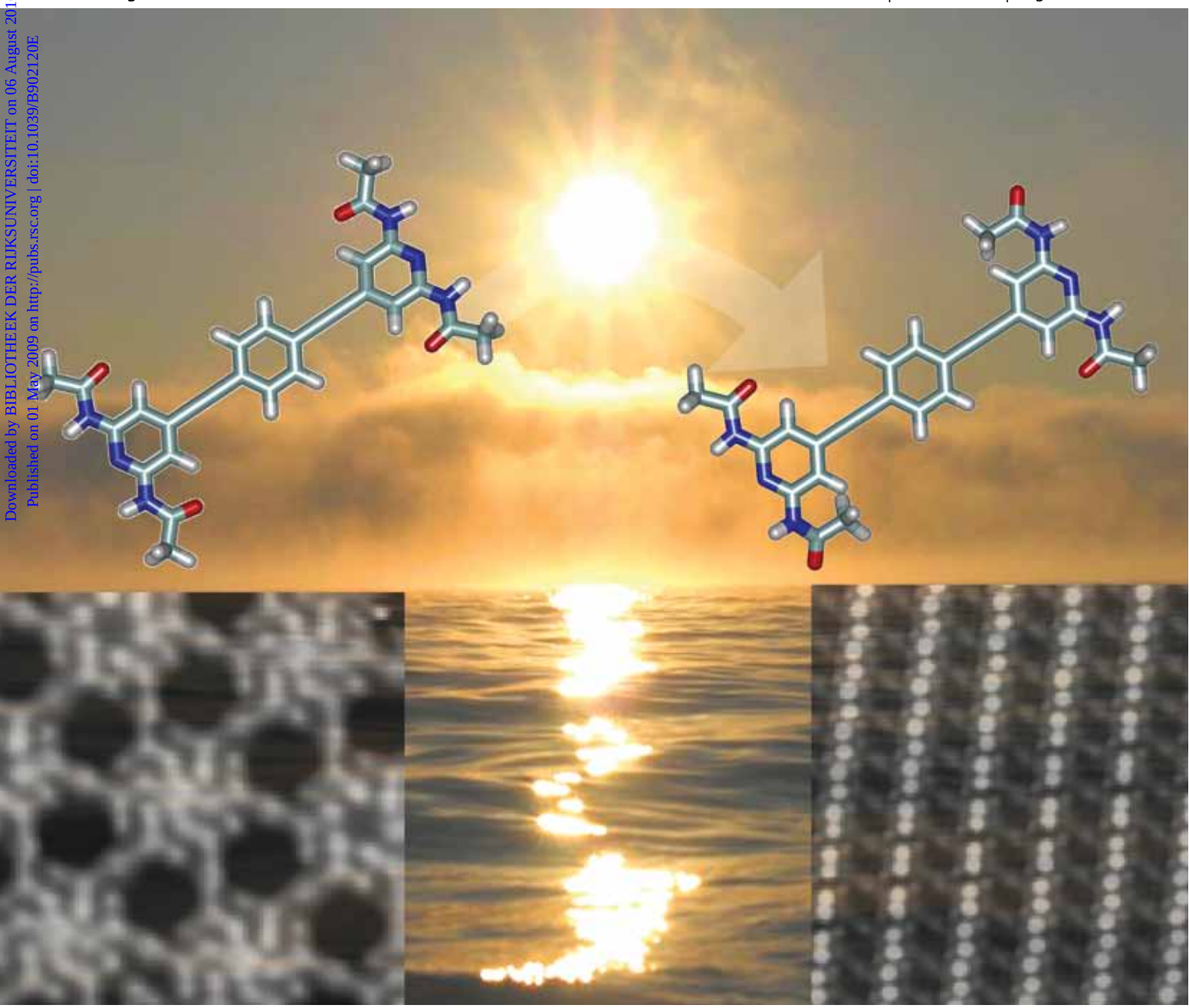

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Davide Bonifazi *et al.*

Conformation-controlled networking of *H*-bonded assemblies on surfaces

Conformation-controlled networking of *H*-bonded assemblies on surfaces†

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A temperature-induced phase transition of a 2D *H*-bonded assembly, enabling quadruple *H*-bonding interactions, from a hexagonal porous network into a close-packed rhombic arrangement has been observed on Ag(111) by STM imaging.

Tailor-made molecules engineered for the creation of supramolecular structures[1] *via* molecular self-assembly[2] may feature conformational degrees of freedom, which allow for the tuning of their pre-programmed intermolecular interactions. So far, only a few studies addressed the investigation of the conformational flexibility of adsorbed organic molecules[3–10] or the influence of the substrate on the conformational state.[11–13] However, networks that could undergo phase transitions through a thermally-induced change of the molecular conformation leading to a variation of the intermolecular interactions have not yet been reported. In order to prepare such networks,[14,15] directional intermolecular forces, such as *H*-bonding interactions, are promising candidates since their strength and geometry can be controlled by the number and the arrangement of the available *H*-bonding donor (*D*) or acceptor (*A*) moieties.[16] Herein, we report on the formation of an *H*-bonded porous network that, upon thermally-induced *trans–cis* inversion of the conformation of the amidic groups, evolves into a close-packed rhombic pattern.

For our studies, the conjugated molecular module **1** bearing two terminal 2,6-di(acetylamino)pyridine recognition sites,[17] which are connected to a 1,4-disubstituted central phenyl ring (Fig. 1d), was used. The terminal group is well-known to be involved in *H*-bonding interactions featuring a DAD conformation.[18] In principle, both *trans* and *cis* conformations (around the CO–NHR bond) of the amidic functional groups are possible but, due to hyperconjugation effects and steric demands, the *trans* conformation is preferred[19] (the calculated ΔH° of the DADA and ADAD conformers are 18.9 and 41.8 kJ mol^{-1} higher than that of the reference DAD unit, Scheme 1).

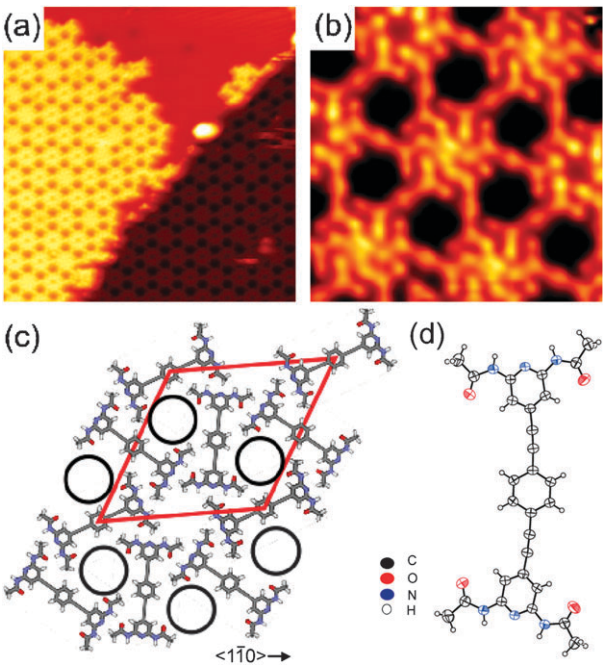
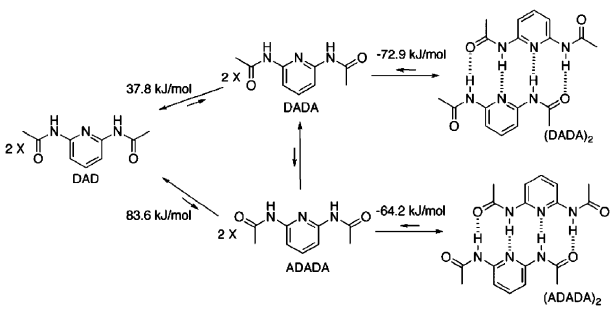


Fig. 1 (a), (b) STM images of **1** on Ag(111) showing the porous network (a: 34 × 34 nm^2 b: 7 × 7 nm^2; V_{bias} = −1.7 V, I_t = 20 pA, T = 77 K). (c) Proposed model. The red rhombus indicates the unit cell, the black circles highlight the pores and the arrow the high symmetry direction of Ag(111). (d) X-ray structure of molecule **1**.



Scheme 1 Influence of the *cis* and *trans* conformers on the dimerisation processes. Calculated ΔH° for conformational changes and dimerisation in the vacuum using MP2/6-311G** level of approximation on B3LYP/6-311G**-optimised geometries as implemented in Gaussian 03.

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† Electronic supplementary information (ESI) available: Experimental section, X-ray crystal structure determinations, computational studies, LEED measurements for molecule **1** on Ag(111). See DOI: 10.1039/b902120e

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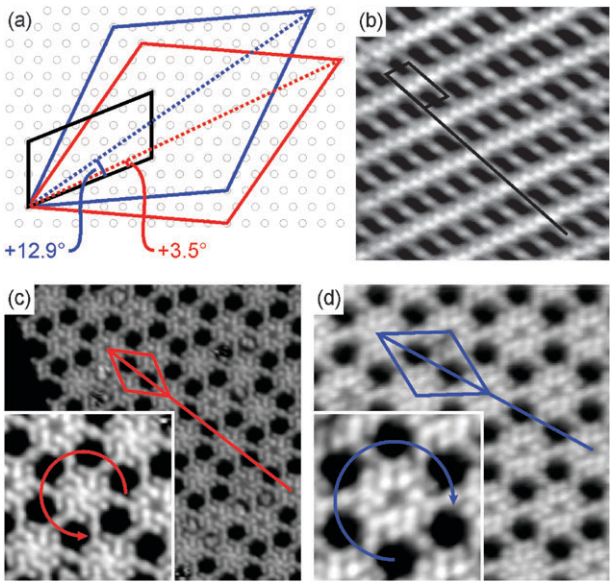

Fig. 2 (a) Unit cell of the close-packed assembly (in black) and of the porous network with its mirrored counterpart (in blue and red, respectively). (b) STM image of the close-packed assembly (10×10 nm^2; $V_{bias} = -1$ V, $I_t = 20$ pA). (c–d) STM images of the porous network, (c) 20×20 nm^2, inset: 6.9×6.9 nm^2, $V_{bias} = -1.7$ V, $I_t = 20$ pA, (d) 12.4×12.4 nm^2, inset 4.6×4.6 nm^2, $V_{bias} = -1.3$ V, $I_t = 20$ pA. Both insets indicate the chirality of the porous network thus allowing to distinguish between mirrored patterns. The angles between the close-packed assembly and the porous network were determined by STM: (c) $+3.8°$ (red angle) and (d) $+13.0°$ (blue angle) and agree very well with the angles obtained from the LEED analysis.

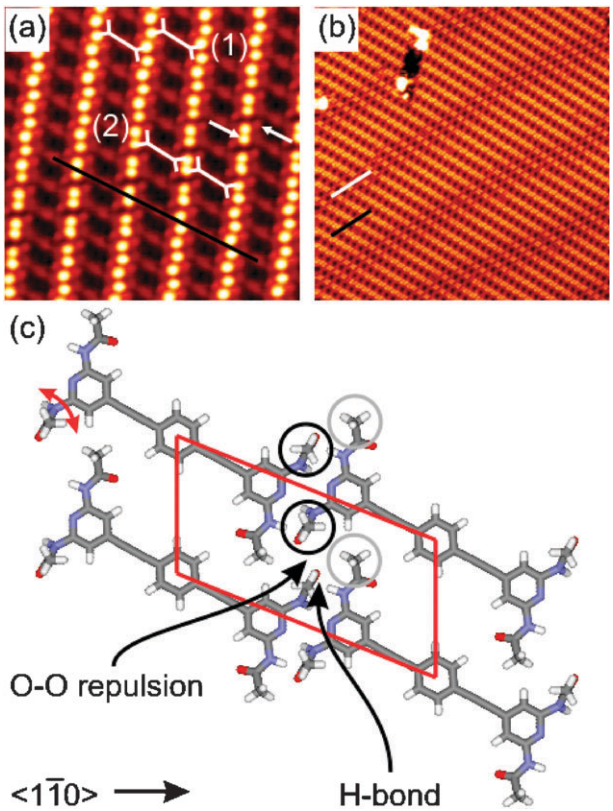

Fig. 3 (a), (b) STM images (a: 10×10 nm^2, $V_{bias} = -2$ V, $I_t = 12$ pA, $T = 77$ K; b: 39×39 nm^2, $V_{bias} = -1.5$ V, $I_t = 12$ pA, $T = 77$ K) of **1** on Ag(111) after thermal annealing at 420 K. The black and white bars in (b) represent areas with optimised O–O distance and *H*-bond length, respectively. (c) Proposed model for the close-packed assembly (see ESI†).

In a first step, the self-organisation of molecule **1** on Ag(111) was investigated under ultrahigh vacuum (UHV) conditions with scanning tunneling microscopy (STM) for coverages ≤ 1 monolayer. For samples prepared at rt, the molecules arrange in a porous hexagonal network (Fig. 1a–b). In high-resolution STM images each molecule is displayed as three aligned lobes and four terminal spokes that correspond to the aromatic rings and the acetyl residues, respectively. In addition, low-energy electron diffraction (LEED) measurements (see ESI†) were performed to determine the size of the unit cell with respect to the underlying Ag(111) substrate. A commensurate superstructure has been found with the molecules arranged in a rhombic unit cell with dimensions of 30.4×30.4 Å^2 and an angle of 60° (Fig. 2a). In the proposed structure (Fig. 1c), for each molecule the four amidic groups are in *trans* conformations (*i.e.*, DAD), as observed in the solid state (Fig. 1d).[18]

In the proposed model, each 2,6-di(acetylamino)pyridine residue interacts *via* two weak *H*-bonds with two neighbouring moieties, which results in the formation of chiral hexameric units (Fig. 2c–d). Consequently, each chiral pore is surrounded by three molecules exhibiting an angle of 60° relative to each other, (Fig. 1c) and it is internally decorated by the 1,4-disubstituted phenyl spacers and the carbonyl groups. A value of 2.0 Å for the CO···H distance was measured, which closely resembles that estimated from the computational simulations (2.05 Å). Remarkably, after annealing the sample at 420 K, the hexagonal network was transformed into the close-packed 2D rhombic pattern shown in Fig. 3a–b. Notably, the intensity corresponding to the two acetyl units of the terminal 2,6-di(acetylamino)pyridine groups varies: one acetyl unit appears always brighter than the other one (white arrows in Fig. 3a), clearly indicating a conformational difference between the two acetyl groups.

Both STM and LEED measurements support the arrangement of **1** in a commensurate superstructure with dimensions of 20.2×10.0 Å^2 with an angle of 68.2° (Fig. 2a–b). In the proposed model, each molecule interacts with two neighbouring modules along the long axis of the unit cell *via* quadruple *H*-bonds, *i.e.* in a head-to-head fashion over their terminal 2,6-di(acetylamino)pyridine groups (Fig. 3c). This intermolecular interaction is equivalent to the one for the $(DADA)_2$ dimers (Scheme 1), where the *cis*-conformation adopted by two of the four amidic bonds strongly promotes frontal *H*-bonding interactions favouring an unidirectional anisotropy. To shed further light upon the origin of the conformational-based self-assembly mechanism, theoretical simulations for single 2,6-di(acetylamino)pyridine units have been performed. Specifically, the conformers displaying a linear DADA arrangement, *i.e.* having one amidic group in the *cis*-conformation, are capable of forming four *H*-bonds in dimeric $(DADA)_2$ species, which is in noticeable contrast to the DAD conformers. Quadruple *H*-bonding interactions can be also extended to ADADA conformers *via* the formation of

$(ADADA)_2$ complexes, in which all amidic groups are in the *cis*-conformation, as observed for acylated 2,4-diamino-*s*-triazines.[18] As estimated from theoretical calculations, starting from two DADA conformers, the *H*-bonded $(DADA)_2$ dimer is stabilised by 72.9 kJ mol^{-1} (*H*-bonding distances/angles amount to 1.85 Å/132° for CO···H–N and to 2.41 Å/124° for C–N···H), which corresponds to a stabilisation enthalpy of 35 kJ mol^{-1} with respect to two free DAD units. The ADADA conformers can also self-assemble into dimers $(ADADA)_2$, but the resulting ΔH° of dimerisation is 19.4 kJ mol^{-1} higher than that of a DAD pair, which makes this arrangement thermodynamically disfavoured (see computational studies, ESI†).

The amide unit in the *cis* conformation displays some flexibility due to a unique type of interplay to control the delicate balance between attractive (*H*-bonds) and repulsive (steric demands) interactions. Depending on which interaction is better minimised, the conformation of the amidic group is slightly distorted and thus, the lateral position of the methyl group is affected (indicated by sketches (1) and (2) in Fig. 3a). In other words: if the NH···O *H*-bond length between two neighbouring molecules in one row (black line in Fig. 3a) is optimised, the O···O repulsion between neighbouring COMe groups is increased and *vice versa* (black arrows in Fig. 3c). It follows that the methyl group in the *cis* conformation has to be lifted from the surface. This explains the differences in brightness observed in the STM images (white arrows in Fig. 3a): the methyl fragments of the amidic groups in the *cis* conformation (indicated as black circles in Fig. 3c) appear brighter than the methyl fragments in the *trans* conformation (indicated as grey circles in Fig. 3c). Since both structures are commensurate to the Ag(111) substrate it can be ruled out that the molecule–substrate interactions are responsible for the transition. Hence, the transition from the porous network to the close-packed assembly is mainly governed by the temperature induced *trans–cis* inversion, as the system tends to minimise its free surface energy. Moreover, both theoretical and experimental results suggest that the formation of the hexagonal network is kinetically controlled while the rhombic assembly represents the thermodynamically stable phase.

In summary, we have demonstrated that, by choosing the recognition moieties appropriately, it is possible to thermally induce a phase transition for a 2D porous assembly (from a hexagonal to a rhombic pattern) by exploiting conformational degrees of freedom. Specifically, we could induce the formation of quadruple *H*-bonds between 2,6-di(acylamino)pyridine moieties through the conformational *trans–cis* inversion of amidic functional groups which is not possible in solution. Control over the conformational state of adsorbed molecules could play an important role in the design of writeable organic-based nanostructures.

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